

**Method for coating metallic surfaces with a mixture
containing at least two silanes**

The invention relates to a process for coating metallic
5 surfaces with an aqueous composition comprising at
least one fluorine-free silane and at least one
fluorine-containing silane and, if desired, organic
film formers and/or further components. The invention
further relates to such aqueous compositions and also
10 to the use of the substrates coated by the process of
the invention.

The processes employed most frequently to date for the
surface treatment or pretreatment prior to coating of
15 metals, particularly of metal strip, are based on the
use of chromium(VI) compounds together with a variety
of additives. In view of the toxicological and
environmental risks associated with such processes and
in view, moreover, of the foreseeable statutory
20 restrictions governing the application of processes
involving chromate, the search has been on for some
time for alternatives to these processes across all
fields of metal surface treatment.

25 The use of silanes in aqueous compositions for
producing siloxane-rich corrosion-protective coatings
is known in principle. Although these coatings have
become established, the processes for coating with an
aqueous composition predominantly comprising silane are
30 in some cases difficult to implement. This coating is
not always formed with ideal properties. In addition
there may be problems in the ability sufficiently to
characterize the very thin, transparent silane coatings
on the metallic substrate, and defects therein, with
35 the naked eye or with optical aids. Corrosion
protection and film adhesion of the siloxane-rich
coatings formed are often high, though not always so,
and in some cases are not high enough for certain

applications even when the coatings are appropriately applied.

5 In the context of the design of silane-containing aqueous compositions, moreover, it has been found appropriate to add a small or large amount of at least one component selected from the group consisting of monomers, oligomers and polymers. With compositions of this kind the nature and amount of the silane added are
10 sometimes critical to a successful outcome. Normally, however, the amounts of silane added for the purpose are comparatively low - often only up to 5% by weight - and in that case act as a coupling agent, where the intention is that it is the adhesion-promoting
15 (coupling) effect in particular between the metallic substrate and coating material and, where appropriate, between pigment and organic coating-material constituents that should prevail, although to a minor extent in some cases there may also be a slight
20 crosslinking effect. Additions of silane are made predominantly to thermally curable resin systems.

Also known, furthermore, are resin mixtures in which resins are blended with inorganic acids in order
25 thereby to obtain a pickling attack and hence improved contact of the resin film directly with the metallic surface. These compositions have the drawback that contamination occurs owing to the pickling attack while the treatment liquid (dispersion) is being contacted
30 with the substrate. This contamination leads to the accumulation of metals in the treatment liquid and consequently to a permanent change in the chemical composition of the treatment liquid, thereby significantly impairing the corrosion protection.
35 These metals are leached by the pickling attack from the metallic surface of the substrates to be treated.

WO 00/46310 teaches a process for coating metallic surfaces with a liquid composition which comprises a hydrolyzed aminosilane and a hydrolyzed multi-silyl-functional silane, but no fluorine-containing silane.

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DE-A1-101 49 148 describes aqueous coating compositions based on organic film former, fine inorganic particles and also lubricants and/or organic corrosion inhibitor, the compositions providing outstanding results in corrosion resistance, adhesion and formability, not least on Galvalume® steel sheets, despite the absence of chromium compounds, but nevertheless also exhibiting inadequate corrosion resistance as an organic film approximately 1 µm thick on hot-dip-galvanized, electrolytically galvanized or Galfan®-coated metallic strips, i.e. on metallic surfaces which are difficult to protect against corrosion. The compositions, their constituents and the properties of the raw materials and coatings in that publication are expressly incorporated by reference into this specification.

The subject matter of German patent application DE 103 08 237 of 25.02.2003, relating to compositions of similar constitution and to corresponding processes for coating metallic surfaces, is explicitly incorporated by reference in terms of the raw materials and their properties, the preparation of the compositions and/or the hydrolyzing of the silanes, the compositions such as concentrates and baths and their properties, the effects, the formation of the coatings such as the drying, filming and curing, for example, the compositions and the properties of the coatings formed, and also the variants of the processes.

It is an object of the invention to overcome the drawbacks of the prior art and in particular to propose a process for coating metallic surfaces which is suitable for coating parts and for coating metallic

strips at high coating speeds, which can be employed substantially or entirely free from chromium(VI) compounds, and which is extremely easy to employ industrially.

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It has surprisingly been found that the addition even of a comparatively small amount of a fluorine-containing silane to an aqueous composition allows coatings to be produced which are much more hydrophobic and corrosion-resistant than comparable coatings without the addition of fluorine-containing silane, without thereby substantially impairing the water-solubility of the composition or its stability. Normally the expectation would be that the more hydrophobic composition would also lead to a distinct deterioration in water-solubility.

The object is achieved with a process for coating a metallic surface, in particular of aluminum, iron, copper, magnesium, nickel, titanium, tin, zinc or alloys containing aluminum, iron, copper, magnesium, nickel, titanium, tin and/or zinc, with an aqueous composition, also comprising, if desired, organic solvent and other components, which is substantially or entirely free from chromium(VI) compounds, for the purpose of pretreatment prior to a further coating or for treatment, where the article to be coated - in particular a strip or strip section - is, if desired, formed after coating, which process is characterized in that the composition comprises, besides water,

- a) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-free silane and
- b) at least one hydrolyzable and/or at least partly hydrolyzed fluorine-containing silane,

the silanes in the composition being water-soluble or becoming water-soluble in particular by virtue of (further) hydrolysis reactions and/or chemical reactions prior to application to the metallic surface,

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the clean, pickled, cleaned and/or pretreated metallic surface being contacted with the aqueous composition and a film being formed on the metallic surface and subsequently dried and, if desired, additionally cured,

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the dried and, where appropriate, also cured film having a thickness in the range from 0.001 to 10 μm , determined by detaching a defined area of the cured film and weighing it or by determining the silicon content of the coating by X-ray fluorescence analysis, for example, and converting accordingly.

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The object is also achieved by aqueous compositions corresponding to claim 26.

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The dependent claims develop the process further. Uses can be found in claim 27 and claim 28.

The silane is characterized in this specification by the dominant constituent of the products, which are generally available commercially. The silanes present in the aqueous composition (concentrate or bath) are monomers, oligomers, polymers, copolymers and/or reaction products with further components as a result of hydrolysis reactions, condensation reactions and/or further reactions. The reactions take place primarily in solution, in the course of the drying and, where appropriate, curing of the coating. The term "silane" is utilized in this context for silanes, silanols, siloxanes, polysiloxanes and their reaction products and/or derivatives, which are often "silane" mixtures. In view of the often highly complex chemical reactions which occur in this context, and in view of highly

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complex analyses and operations, it is not possible to specify the particular further silanes and other reaction products.

- 5 The silanes for the purposes of this specification are regarded as being water-soluble if they summarily at room temperature in the silane composition have a solubility in water of at least 0.05 g/l, preferably at least 0.1 g/l, more preferably at least 0.2 g/l or at
10 least 0.3 g/l. This does not imply that every single one of these silanes must have this minimum solubility but rather that these minimum values are achieved on average.
- 15 In the aqueous composition preferably there is at least one silane selected from the fluorine-free silanes: from in each case at least one acyloxysilane, alkoxysilane, silane having at least one amino group such as an aminoalkylsilane, silane having at least one
20 succinic acid group and/or succinic anhydride group, bis-silyl-silane, silane having at least one epoxy group such as a glycidyloxysilane, (meth)acrylato-silane, multi-silyl-silane, ureidosilane, vinylsilane and/or at least one silanol and/or at least one
25 siloxane or polysiloxane whose composition corresponds chemically to that of the aforementioned silanes. It comprises at least one silane and/or (in each case) at least one monomeric, dimeric, oligomeric and/or polymeric silanol and/or (in each case) at least one
30 monomeric, dimeric, oligomeric and/or polymeric siloxane, the term "oligomers" being intended here to embrace even trimers.

In particular therein there is at least one fluorine-
35 free silane selected from the group consisting of, or based on,

glycidyloxyalkyltrialkoxysilane,

methacryloyloxyalkyltrialkoxysilane,
(trialkoxysilyl)alkylsuccinoysilane,
aminoalkylaminoalkylalkyldialkoxysilane,
(epoxycycloalkyl)alkyltrialkoxysilane,
bis(trialkoxysilylalkyl)amine,
bis(trialkoxysilyl)ethane,
(epoxyalkyl)trialkoxysilane,
aminoalkyltrialkoxysilane,
ureidoalkyltrialkoxysilane,
N-(trialkoxysilylalkyl)alkylenediamine,
N-(aminoalkyl)aminoalkyltrialkoxysilane
N-(trialkoxysilylalkyl)dialkylenetriamine,
poly(aminoalkyl)alkyldialkoxysilane,
tris(trialkoxysilyl)alkyl isocyanurate,
ureidoalkyltrialkoxysilane and
acetoxysilane.

With particular preference therein there is at least one silane selected from the group consisting of, or based on,

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3-glycidyloxypropyltriethoxysilane,
3-glycidyloxypropyltrimethoxysilane,
3-methacryloyloxypropyltriethoxysilane,
3-methacryloyloxypropyltrimethoxysilane,
3-(triethoxysilyl)propylsuccinoysilane,
aminoethylaminopropylmethyldiethoxysilane,
aminoethylaminopropylmethyldimethoxysilane,
beta-(3,4-epoxycyclohexyl)ethyltriethoxysilane,
beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane,
beta-(3,4-epoxycyclohexyl)methyltriethoxysilane,
beta-(3,4-epoxycyclohexyl)methyltrimethoxysilane,
gamma-(3,4-epoxycyclohexyl)propyltriethoxysilane,
gamma-(3,4-epoxycyclohexyl)propyltrimethoxysilane,
bis(triethoxysilylpropyl)amine,
bis(trimethoxysilylpropyl)amine,
(3,4-epoxybutyl)triethoxysilane,
(3,4-epoxybutyl)trimethoxysilane,

gamma-aminopropyltriethoxysilane,
gamma-aminopropyltrimethoxysilane,
gamma-ureidopropyltrialkoxysilane,
N-(3-(trimethoxysilyl)propyl)ethylenediamine,
N-beta-(aminoethyl)-gamma-aminopropyltriethoxysilane,
N-beta-(aminoethyl)-gamma-aminopropyltrimethoxysilane,
N-(gamma-triethoxysilylpropyl)diethylenetriamine,
N-(gamma-trimethoxysilylpropyl)diethylenetriamine,
N-(gamma-triethoxysilylpropyl)dimethylenetriamine,
N-(gamma-trimethoxysilylpropyl)dimethylenetriamine,
poly(aminoalkyl)ethyldialkoxysilane,
poly(aminoalkyl)methyldialkoxysilane,
tris(3-(triethoxysilyl)propyl) isocyanurate,
tris(3-(trimethoxysilyl)propyl) isocyanurate and
vinyltriacetoxysilane.

Preferably in the aqueous composition there is at least one silane selected from the fluorine-containing silanes: from in each case at least one acyloxysilane,
5 alkoxy silane, silane having at least one amino group such as an aminoalkylsilane, silane having at least one succinic acid group and/or succinic anhydride group, bis-silyl-silane, silane having at least one epoxy group such as a glycidyloxysilane, (meth)acrylato-
10 silane, multi-silyl-silane, ureidosilane, vinylsilane and/or at least one silanol and/or at least one siloxane or polysiloxane whose composition corresponds chemically to that of the aforementioned silanes, containing in each case at least one group that
15 contains one, or contains at least one, fluorine atom.

In particular the aqueous composition comprises at least one fluoroalkoxyalkylsilane, at least one mono-, di- or trifunctional fluorosilane, at least one mono-,
20 bis- or tris-fluorosilane, at least one fluorosilane based on ethoxysilane and/or based on methoxysilane and/or at least one fluorosilane having at least one functional group such as, for example, an amino group,

in particular in the form of a cocondensate, such as, for example, a fluoroalkyldialkoxysilane, a fluoro-aminoalkylpropyltrialkoxysilane, a fluoromethanesulfonate, a fluoropropylalkyldialkoxysilane, a triphenyl-
5 fluorosilane, a trialkoxylfluorosilane, a trialkylfluorosilane and/or a tridecafluorooctyltrialkoxysilane.

With particular preference the composition comprises at
10 least one silane that contains at least two amino groups and also at least one ethyl group and/or at least one methyl group.

The amount of all silanes a) and b), including any
15 reaction products formed with other components, is together preferably from 0.01 to 100 g/l in a concentrate or from 0.002 to 12 g/l in a bath. In the case of a concentrate this amount is more preferably in the range from 0.05 to 80 g/l, very preferably in the
20 range from 0.1 to 60 g/l, in particular roughly 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 20, 22.5, 25, 27.5, 30, 35, 40, 45, 50 or 55 g/l. In the case of a bath this amount is more preferably in the range from 0.005 to 5 g/l, very preferably in the
25 range from 0.01 to 3 g/l, in particular roughly 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 2.0, 2.25, 2.5 or 2.75 g/l. Dilution of the concentrate, which is normally carried out with water and only occasionally
30 with a mixture of water and at least one organic solvent, can be carried out in particular by a factor of from 1.5 to 30, frequently by a factor of from 2 to 20, in particular by a factor of from 3 to 12.

35 The proportion of a) to b) is preferably in each case in the range from 1:0.01 to 1:4, more preferably in a proportion of from 1:0.03 to 1:3, very preferably in a proportion of from 1:0.05 to 1:2.5 and in particular is

in each case at least 1:0.08, 1:0.12, 1:0.16, 1:0.2, 1:0.25, 1:0.3, 1:0.35, 1:0.4, 1:0.45 or 1:0.5 or in particular in each case up to 1:2.5, 1:2.2, 1:2, 1:1.8, 1:1.6, 1:1.4, 1:1.2, 1:1.1, 1:1, 1:0.9, 1:0.8, 1:0.7 or
5 1:0.6. The particular optimum of this proportion may fluctuate, however, according to which silanes a) and b) are used and how they are hydrolyzed.

Preferably an aqueous composition is selected on the
10 criteria that more than 60% by weight, in particular more than 80% by weight of the silanes have good water-solubility and that the composition prepared therewith in the form of a concentrate or bath possesses good stability for the time of processing. This processing
15 time may vary between 2 hours and 6 months according to requirements. Good stability here means that the composition undergoes only slight precipitation, if any at all, and only slight chemical and/or physical change, if any at all. The composition composed
20 essentially of silanes and solvents is preferably clear. In this context it is preferred to select those silanes and those reactions and process steps such that the compounds formed from the silanes in such reactions/steps adopt structures which can be regarded
25 as ladder structures to a relatively large extent, in particular predominantly or even extensively.

It can be particularly preferable to add at least two different fluorine-free silanes, possibly even three or
30 four different fluorine-free silanes, to the aqueous composition. Among the many possible combinations it is particularly preferred to use a combination of at least one functional trialkoxysilane and at least one bis-trialkoxysilane, of at least one aminosilane and at
35 least one bis-trialkoxysilane, of at least one bis-trialkoxysilane and of at least one vinylsilane, of at least one bis-trialkoxysilane and of at least one ureidosilane, of at least one vinylsilane and of at

least one bis-trialkoxysilylpropylsilane, of at least one aminoalkylsilane and of at least one bis-trialkoxysilylpropylsilane, of at least one bis-trialkoxysilylpropyltetrasulfane and of at least one bis-trialkoxysilylpropylsilane, of at least one fluorine-free silane containing cyano and/or epoxy groups with a fluorine-free silane different therefrom, with the addition if desired of additionally at least one ureidosilane, at least one multi-silyl-silane, at least one bis-trialkoxysilylpropyltetrasulfane and/or at least one further trialkoxysilane to one of these combinations.

It can also be particularly preferred to add at least two different fluorine-containing silanes, possibly even three or four different fluorine-containing silanes, to the aqueous composition.

Particular preference is given to a combination of in each case at least one organosilane, one organofunctional silane and one fluoro-silane, in particular of in each case at least one aminosilane, one multi-silyl-silane and one fluoro-silane.

It may be advantageous to hydrolyze the individual silanes, where they are not already sufficiently hydrolyzed, only individually, to store them individually where appropriate and then to add them to the composition. Chemical reactions or condensation reactions may also take place during the time of hydrolysis. Even after that time, however, it is possible for the hydrolysis and/or the chemical reactions or condensation reactions to proceed further, where appropriate in the course of storage, but in some cases even following addition to the composition in the concentrate or bath.

The aqueous composition, which in this specification is referred to as a solution, need not be a solution in

the strict sense, especially since it is often possible only by means of additional analyses to determine whether the solutions in question are true solutions. In particular the aqueous composition may also be a
5 suspension and/or emulsion, especially when particles, particularly inorganic particles, are added.

The aqueous composition comprises as solvent at least water, the water content in the solvent mixture being
10 more than 50% by weight in the case of a concentrate and more than 75% by weight in the case of a bath composition. The amount of water in the solvent mixture in the case of a concentrate is preferably at least 60% by weight, more preferably at least 70% by
15 weight, very preferably at least 80% by weight, in particular at least 90% by weight. The amount of water in the solvent mixture in the case of a bath composition is preferably at least 80% by weight, more preferably at least 85% by weight, very preferably at
20 least 90% by weight, in particular at least 95% by weight. The amount of further solvents other than water, in other words particularly of organic solvents such as ethanol, methanol, propanol and/or isopropanol, for example, may on the one hand be added to the
25 concentrate or to the bath and/or may be formed in the concentrate or bath by chemical reactions. For reasons of environmental protection, however, it is preferred that the content of organic solvents be kept as low as possible. For process engineering reasons a certain
30 organic solvent content or low organic solvent content is sometimes preferred, but in some cases, owing to chemical reactions, it is unavoidable unless the organic solvent is removed artificially afterwards.

35 The aqueous composition contains not more than 0.2 g/l chromium, preferably not more than 0.1 g/l chromium, more preferably not more than 0.02 g/l chromium, the chromium content possibly originating in particular

from entrainments and/or from etching operations on chromium-containing alloys and/or chrome plating. Preferably there are also no contents of further heavy metals, besides iron, manganese and zinc, that total
5 more than 0.8 g/l.

In a first particularly preferred variant of this invention the aqueous composition comprises the silanes a) and b), water and, if desired, at least one organic
10 solvent such as methanol, ethanol, isopropanol and/or propanol, for example, at least one alkaline agent such as ammonia, for example, at least one acidic agent such as acetic acid and/or glacial acetic acid, for example, at least one surfactant to reduce the surface tension
15 and for uniformly and reliably coating the metallic surface, such as at least one nonionic, at least one anionic, at least one cationic and/or at least one amphoteric surfactant, for example, and/or at least one additive such as at least one preservative and/or at
20 least one biocide, for example.

The bath compositions of the aqueous compositions predominantly comprising silanes preferably have a water content in the range from 80 to 99.9% by weight, more preferably in the range from 90 to 99.8% by
25 weight, very preferably in the range from 94 to 99.7% by weight, particularly in the range from 96 to 99.6% by weight, in particular about 91, 91.5, 92, 92.5, 93, 93.5, 94, 94.5, 95, 95.5, 96, 96.5, 97, 97.5, 97.9, 98.2, 98.5, 98.8, 99.1 or 99.4% by weight.
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The amounts of further components besides silanes and solvents in the bath are normally not more than 5 g/l in total, preferably not more than 3 g/l in total, more
35 preferably not more than 1.5 g/l, but in the concentrate may be higher accordingly.

In a second and a third particularly preferred variant of this invention at least one component selected from the eleven components below is added additionally to the compositions of the first particularly preferred variant:

- c) metal chelate,
- d) monomer, oligomer, polymer and/or copolymer,
- e) selected from at least one of the following components
 - e₁) at least one inorganic compound in particle form, having an average particle diameter, measured on a scanning electron microscope, in the range from 0.005 to 0.3 μm in diameter,
 - e₂) at least one lubricant,
 - e₃) at least one organic corrosion inhibitor,
 - e₄) at least one anti-corrosion pigment,
 - e₅) at least one agent for neutralizing and/or sterically stabilizing the synthetic resins,
 - e₆) at least one organic solvent,
 - e₇) at least one siloxane,
 - e₈) at least one long-chain alcohol, and
 - e₉) at least one surfactant.

Particular preference is given to amounts of chelate(s), in each case including the resultant reaction products, of from 0.01 to 15% by weight, based on the solids content of the bath composition, more preferably, in each case independently of one another, amounts of from 0.03 to 11% by weight, in particular roughly amounts, independently of one another in each case, of 0.05, 0.1, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10 or 10.5% by weight.

Preferably at least one silane is selected that is compatible with water, i.e. such that the at least one silane and/or, where appropriate, its hydrolysis and condensation products are miscible with the components
5 of the aqueous composition, without disruption, and have a keeping duration of at least several weeks, and that it allows the formation of a defect-free wet film and dry film which in particular is coherent, uniform and free from craters. Selected in particular is at
10 least one silane which enables high corrosion resistance in particular in combination with the selected, at least one chelate.

Preferably at least one chelate is selected which
15 behaves stably in aqueous dispersions in the presence of the other components of the aqueous composition for a number of days or weeks and which enables a high corrosion resistance. In addition it is advantageous if not only the at least one silane but also the at
20 least one chelate are able to attach chemically to the envisaged metal surface that is to be contacted therewith and where appropriate are likewise able to attach chemically to the coating material to be applied subsequently. The at least one metal chelate is in
25 particular one of Al, B, Ca, Fe, Hf, La, Mg, Mn, Si, Ti, Y, Zn, Zr and/or at least one lanthanide such as Ce or such as a Ce-containing lanthanide mixture, selected with particular preference from the group consisting of Al, Hf, Mn, Si, Ti, Y and Zr.

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The concentrates of the aqueous compositions comprising predominantly silanes and also chelate(s) and also of the part-components as a starting product of polymer-containing compositions preferably have a water content
35 in the range from 20 to 95% by weight, in particular from 30 to 90% by weight. The concentrates preferably comprise the silanes, including the reaction products formed therefrom, in an amount in the range from 0.1 to

- 60% by weight, more preferably in the range from 0.2 to 45% by weight, very preferably in the range from 0.3 to 35% by weight, in particular in the range from 0.5 to 32% by weight, especially of about 0.8, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22.5, 25, 27.5 or 30% by weight, and preferably comprise the at least one chelate, including any reaction products formed therefrom, in the range from 0.1 to 50% by weight, more preferably in the range from 0.2 to 40% by weight, very preferably in the range from 0.3 to 30% by weight, in particular in the range from 0.5 to 25% by weight, especially of about 0.75, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20 or 22.5% by weight.
- 15 The bath compositions of the aqueous compositions comprising predominantly silane and chelate preferably have a water content in the range from 80 to 99.9% by weight, which may also include a fraction of at least one organic solvent. The amount of water and/or at least one organic solvent is preferably in the range from 90 to 99.8% by weight, more preferably in the range from 94 to 99.7% by weight, in particular in the range from 96 to 99.6% by weight, especially of about 95, 95.5, 96, 96.5, 97, 97.5, 97.9, 98.2, 98.5, 98.8, 99.1 or 99.4% by weight.

The bath compositions preferably comprise the silanes, including any reaction products formed therefrom with other components, in an amount in the range from 0.01 to 10% by weight, more preferably in the range from 0.05 to 7% by weight, very preferably in the range from 0.1 to 5% by weight, in particular in the range from 0.2 to 4% by weight, especially of about 0.4, 0.6, 0.8, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6 or 3.8% by weight, and preferably comprise the at least one chelate, including any reaction products formed therefrom, in the range from 0.01 to 10% by weight,

more preferably in the range from 0.05 to 7% by weight, very preferably in the range from 0.1 to 5% by weight, in particular in the range from 0.2 to 4% by weight, especially of about 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, 3.6 or 3.8% by weight.

The amounts of the silanes and of the at least one chelate, including in each case the reaction products formed therefrom, particularly those of titanium, hafnium and/or zirconium, preferably account for at least 20% by weight, in particular at least 30% by weight, more preferably at least 40%, very preferably at least 50% by weight, in particular in each case at least 60, 70, 80, 90, 94, 95, 96, 97, 98 or 99% by weight of the solids contents of this composition. With particular preference this composition is composed essentially of water, in each case at least one silane and/or reaction products thereof, at least one chelate, including any reaction products formed therefrom, and also, if desired, amounts of substances selected from the group consisting of alcohols, acids such as carboxylic acids and fatty acids such as acetic acid and/or mineral acids and other substances which influence pH, such as ammonia, and/or additives and impurities. The total amount of further compounds, including additives, besides silane and chelate is normally up to 20% by weight of the solids content of silane and chelate, preferably up to 15% by weight, more preferably up to 10% by weight, very preferably up to 5% by weight, in particular up to 1 or 2% by weight.

Although the ratio of the at least one silane, including the reaction products formed therefrom, to the at least one chelate, including any reaction products formed therefrom, can preferably be in the range from 0.8:1 to 1.2:1, it has surprisingly become clear that this ratio can also be in particular in the

range from 0.2:1 to 0.5:1 or can be from 2:1 to 5:1, since there may be an optimum there in certain situations.

5 The pH of the bath composition can be in particular in the range from 3 to 9.5, preferably in the range from 3.5 to 9, in particular in the range from 4 to 8.8. In order to adjust the pH it is possible, among other measures, to add an amount of a weak acid or of a
10 dilute strong acid, or an acid mixture. In particular it is possible to use at least one acid such as carboxylic acids or fatty acids such as acetic acid and/or mineral acids and other substances which influence pH, such as ammonia. The bath composition
15 can in some cases be adjusted to pH values about 3.5 units less by addition of acid, if the chemical system withstands the chosen pH and remains stable. Preferably it is also possible to add a solvent such as an alcohol to stabilize the silane.

20 The coatings formed with these bath compositions typically have a film thickness in the range from 0.01 to 0.6 μm , generally from 0.015 to 0.25 μm .

25 As well as the silanes the inventive composition may also comprise monomers, oligomers, polymers and/or copolymers. For the purposes of this specification the term "copolymers" preferably embraces block copolymers and graft copolymers as well.

30 The acid number of the synthetic resins is preferably from 3 to 100, more preferably from 3 to 60 or from 4 to 50. In particular, copolymers having an acid number in the range from 3 to 50 are added to the aqueous
35 composition. Where appropriate, the components of the organic film former that are to be added are already in partly neutralized form. The organic film former may preferably include a fraction of at least one copolymer

having an acid number in the range from 3 to 80, in particular to an extent of at least 50% by weight of the synthetic resins added. Within a high acid-number range it is normally not necessary to stabilize a film former cationically, anionically and/or sterically. In the case of a low acid number, however, such stabilization is often necessary. In that case it is advantageous to use already (partly) stabilized synthetic resins and/or mixtures thereof.

The aqueous composition preferably comprises at least one synthetic resin such as organic polymer, copolymer and/or mixture thereof, in particular a synthetic resin based on acrylate, ethylene, polyester, polyurethane, silicone-polyester, epoxide, phenol, styrene, melamine-formaldehyde, urea-formaldehyde and/or vinyl. The organic film former may preferably comprise a synthetic resin mixture of at least one polymer and/or at least one copolymer, comprising, in each case independently of one another, synthetic resin based on acrylate, epoxide, ethylene, urea-formaldehyde, phenol, polyester, polyurethane, styrene, styrene-butadiene and/or vinyl. The film former may also be a cationically, anionically and/or sterically stabilized synthetic resin or polymer and/or a dispersion thereof or even a solution thereof. For the purposes of this specification the term "acrylate" includes acrylic esters, polyacrylic acid, methacrylic esters and methacrylate.

The organic film former may preferably comprise at least one component based on

acrylic-polyester-polyurethane copolymer,
acrylic-polyester-polyurethane-styrene copolymer,
acrylic ester,
acrylic ester-methacrylic ester, if desired with free acids and/or acrylonitrile,

ethylene-acrylic mixture,
ethylene-acrylic copolymer,
ethylene-acrylic-polyester copolymer,
ethylene-acrylic-polyurethane copolymer,
ethylene-acrylic-polyester-polyurethane copolymer,
ethylene-acrylic-polyester-polyurethane-styrene
copolymer
ethylene-acrylic-styrene copolymer,
polyester resins having free carboxyl groups in
combination with melamine-formaldehyde resins,
a synthetic resin mixture and/or copolymer based on
acrylate and styrene,
a synthetic resin mixture and/or copolymer based on
styrene-butadiene,
a synthetic resin mixture and/or copolymer of acrylate
and epoxide,
on the basis of an acrylic-modified carboxyl-
containing polyester together with melamine-
formaldehyde and ethylene-acrylic copolymer,
polycarbonate-polyurethane,
polyester-polyurethane,
styrene,
styrene-vinyl acetate,
vinyl acetate,
vinyl ester and/or
vinyl ether.

The organic film former, however, may also preferably
comprise as synthetic resin an amount of organic
polymer, copolymer and/or mixtures thereof based on
5 polyethyleneimine, polyvinyl alcohol, polyvinylphenol,
polyvinylpyrrolidone and/or polyaspartic acid, in
particular copolymers with a phosphorus-containing
vinyl compound. Preferably a conductive polymer, too,
is added to the aqueous composition.

10

In the second particularly preferred variant of the
invention the weight ratio of compounds of component

d) - monomers/oligomers/polymers/copolymers - to silanes in the concentrate and/or in the bath is preferably in the range from 0.1:1 to 10:1, more preferably in the range from 0.2:1 to 5:1, very preferably in the range from 0.3:1 to 3:1, and in particular is up to 2:1 or up to 1.5:1. In the case of this variant the silanes can act not only and normally only to a minor extent or not at all as a coupling agent.

10

In the third particularly preferred variant of the invention the weight ratio of compounds of component d) - monomers/oligomers/polymers/copolymers - to silanes in the concentrate and/or in the bath is preferably in the range from 3:1 to 200:1, more preferably in the range from 8:1 to 120:1, very preferably in the range from 12:1 to 100:1. In the case of this variant the silanes in many cases act partly, predominantly or wholly only as a coupling agent. In particular in the case of this variant it is frequently advantageous to use a long-chain alcohol e₈) as film-forming assistant, which during the formation of the film provides approximation or alignment of the glass transition temperatures T_g or of the minimum film-formation temperatures MFFT. By this means it is possible for coatings to form which in terms of the organic substances are of particularly homogeneous construction, which has a beneficial effect on the properties of these coatings.

25
30

In one embodiment which is particularly preferred in this context it is possible to use a mixture of organic film formers in which at least one part of the film formers has a glass transition temperature T_g of substantially equal and/or similar T_g . It is particularly preferred here for at least part of the organic film formers to have a glass transition temperature T_g in the range from 10 to 70°C, very

35

- preferably in the range from 15 to 65°C, in particular in the range from 20 to 60°C. The organic film former then preferably comprises at least one fraction of at least one polymer and/or at least one copolymer having
- 5 a minimum film formation temperature MFFT in the range from -10 to +99°C, more preferably in the range from 0 to 90°C, in particular from 5°C onward or from 10°C onward. It is particularly preferred in this case for at least two, if not indeed all, of the organic film
- 10 formers to have a minimum film formation temperature in one of these temperature ranges - provided it is possible to specify a minimum film formation temperature.
- 15 It is particularly advantageous here if all of the organic film formers form films on drying. It is particularly preferred if the aqueous composition is admixed with synthetic resins of which at least 80% by weight have thermoplastic properties, in particular at
- 20 least 90% by weight.

The selection of suitable film-forming assistants in this context is not simple; often a mixture of at least two film-forming assistants is necessary. Particularly

25 advantageous film-forming assistants are what are called long-chain alcohols, particularly those having 4 to 20 carbon atoms, such as a butanediol, a butyl glycol, a butyl diglycol, an ethylene glycol ether such as ethylene glycol monobutyl ether, ethylene glycol

30 monoethyl ether, ethylene glycol monomethyl ether, ethyl glycol propyl ether, ethylene glycol hexyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol butyl ether, diethylene glycol hexyl ether or a polypropylene glycol ether such as

35 propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, tripropylene glycol monomethyl ether, propylene glycol monobutyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monobutyl ether,

propylene glycol monopropyl ether, dipropylene glycol monopropyl ether, tripropylene glycol monopropyl ether, propylene glycol phenyl ether, trimethylpentanediol diisobutyrate, a polytetrahydrofuran, a polyetherpolyol
5 and/or a polyesterpolyol. In contradistinction to film formation, thermally curing organic coatings normally require temperatures of at least 120°C for crosslinking.

10 In a fourth particularly preferred variant of the invention appropriate measures are taken to form a hydrophobic surface which owing to the hydrophobicity and/or the surface microstructure has self-cleaning
15 surface microstructure, through the addition of organic and/or inorganic particles, through formation of organic particles, through the appropriate process regime to obtain a microstructure such that as a result there is structuring in the nanometer and/or micrometer
20 range. The particles which are added preferably possess to a relatively large extent a rough surface and/or a complex geometry and/or associate and/or are associated so as to form aggregates and/or agglomerates which are of complex shape or rough to a greater
25 extent. This process may be assisted by adding particles differing in fineness: that is, particles of different average size and/or different size distribution. The coating produced in this way may preferably have a surface that has a microstructure
30 which is at least partly such that a microstructure is superimposed on a moderately fine microstructure. This coating may be constituted on the basis of the compositions of the particularly preferred first, second or third variant.

35

Furthermore, there are other preferred embodiments in which, in particular, at least one component selected from e₁) to e₉) is present and if desired at least one

of components c) or d) is also present, in addition, if desired, to at least one monomer/oligomer/polymer/copolymer and/or to at least one inorganic compound in particle form.

5

It is preferred as lubricant e₂) to use at least one wax selected from the group consisting of paraffins, polyethylenes and polypropylenes, in particular an oxidized wax, the amount of waxes in the aqueous composition being preferably in the range from 0.01 to 5% by weight, more preferably in the range from 0.02 to 3.5% by weight, very preferably in the range from 0.05 to 2% by weight. The melting point of the wax used as lubricant is preferably in the range from 40 to 165°C, more preferably in the range from 50 to 160°C, and in particular in the range from 120 to 150°C. It is particularly advantageous, in addition to a lubricant having a melting point in the range from 120 to 165°C, to add a lubricant having a melting point in the range from 45 to 95°C or having a glass transition temperature in the range from -20°C to +60°C, in particular in amounts of from 2 to 30% by weight, preferably from 5 to 20% by weight, of the total solids content. This latter lubricant may also be used with advantage alone.

It is particularly advantageous to use the wax in the form of an aqueous dispersion and/or a cationically, anionically and/or sterically stabilized dispersion, since it can then be maintained in homogeneously distributed form in the aqueous composition with ease. The at least one lubricant, which if desired may also at the same time be a forming agent, is preferably present in an amount in the range from 0.1 to 25 g/l and more preferably in an amount in the range from 1 to 15 g/l in the aqueous composition.

The aqueous composition preferably comprises at least one organic corrosion inhibitor e_3), based in particular on amine(s), preferably at least one alkanolamine - preferably a long-chain alkanolamine, at least one TPA-
5 amine complex such as acid adduct-4-oxo-4-p-tolyl butyrate-4-ethylmorpholine, at least one zinc salt of aminocarboxylate, of 5-nitro-isophthalic acid or of cyanic acid, at least one polymeric ammonium salt with fatty acid, at least one metal salt of a sulfonic acid
10 such as dodecyl-naphthalenesulfonic acid, at least one amino complex and transition metal complex of toluenepropionic acid, 2-mercapto-benzothiazolyl-succinic acid and/or of at least one of their amino salts, at least one conductive polymer and/or at least
15 one thiol, it being possible for the amount of organic corrosion inhibitors in the aqueous composition to be situated preferably in the range from 0.01 to 5% by weight, more preferably in the range from 0.02 to 3% by weight, very preferably in the range from 0.05 to 1.5%
20 by weight.

The at least one organic corrosion inhibitor is preferably not highly volatile at room temperature. Further, it may be advantageous if it is readily
25 soluble in water and/or readily dispersible in water, in particular at more than 20 g/l. Particular preference is given, inter alia, to alkylaminoethanols such as dimethylaminoethanol and/or complexes based on a TPA amine such as N-ethylmorpholine complex with
30 4-methyl- γ -oxo-benzenebutanoic acid. This corrosion inhibitor can be added in order to produce greater corrosion inhibition or to make corrosion inhibition even greater.

35 The aqueous composition preferably contains from 0.1 to 80 g/l of the at least one anti-corrosion pigment e_4). These include, in particular, various silicates based on aluminum silicates, aluminosilicates, alumino-

alkaline-earth metal silicates, and alkaline-earth metal silicates. The anti-corrosion pigments preferably have an average particle diameter, measured on a scanning electron microscope, in the range from 5 0.01 to 0.5 μm diameter, in particular in the range from 0.02 to 0.3 μm . The various kinds of anti-corrosion pigments are known in principle. An addition of at least one of these pigments, however, does not appear fundamentally to be necessary, but makes 10 alternative variants possible.

The agents for neutralizing and/or sterically stabilizing the acid groups of the synthetic resins with an acid number in particular in the range from 15 to 50, e_5), may be, inter alia, low-volatility alkanolamines and hydroxides such as sodium hydroxide and potassium hydroxide solutions, but preferably high-volatility alkanolamines, ammonia and compounds based on morpholine and alkanolamines. Their effect is that 20 the neutralized synthetic resins become miscible with water and/or are even soluble in water in the case of an acid number of about 150 or more.

In the process of the invention it is also possible if 25 desired to add at least one organic solvent e_6). As organic solvent for the organic polymers it is possible to use at least one water-miscible and/or water-soluble alcohol, a glycol ether or n-methylpyrrolidone and/or water; where a solvent mixture is used it is possible 30 in particular to use a mixture of at least one long-chain alcohol, such as propylene glycol, an ester alcohol, a glycol ether and/or butanediol, for example, with water. In many cases, however, it is preferred to add only water without any organic solvent at all. 35 Where organic solvent is used its amount is preferably from 0.1 to 10% by weight, in particular from 0.25 to 5% by weight, very preferably from 0.4 to 3% by weight. For strip production it is preferred to use, rather,

only water and almost no organic solvents or none at all, apart possibly from small amounts of alcohol.

- It may further be advantageous to add at least one wetting agent, in order to allow the wet film to be applied uniformly in its two-dimensional extent and in film thickness and also to allow it to be applied coherently and with no defects. In principle a large number of wetting agents are suitable for this purpose, preferably acrylates, silanes, polysiloxanes, and long-chain alcohols, which lower the surface tension of the aqueous composition. Particular preference is given to adding at least one polysiloxane e₇).
- 15 The addition of at least one surfactant e₉) may help to improve the wetting of the composition of the invention on a metallic surface and to improve the coating, in particular to make it more uniform. In this context a distinct improvement can be achieved in particular in the case of surfaces which are particularly rough. Suitability for this purpose is possessed by a very large number of kinds of surfactants, particularly nonionic, cationic, amphoteric and anionic surfactants. A low level of addition in the range from 0.01 to 0.4 g/l is often sufficient.

The compositions of the invention can, furthermore, also be used as an after-rinse solution, following a prior coating operation such as, for example, a conversion coating operation. As a conversion coating it is possible, for example, to apply coatings based on at least one organic and/or inorganic acid, if desired with further adjuvants, based on a phosphating treatment, for example on the basis of iron, calcium, magnesium, manganese and/or zinc, produced on the basis of a complex fluoride-containing solution or dispersion, based on phosphonate, based on at least one silane/siloxane and/or polysiloxane and/or based on

rare earth compounds, to the metallic surfaces first of all. Such solutions or after-rinse solutions may therefore be particularly suitable for bright corrosion protection, where no paint and no paint-like coatings are applied. A conversion coating based on rare earth compounds such as cerium oxide, for example, can be employed in particular on surfaces rich in Al, Mg, Ti and/or Zn.

10 Inventive and comparative examples:

The examples described below are intended to illustrate the subject matter of the invention.

A) Compositions of relatively high silane content:

15

To prepare aqueous concentrates an aqueous mixture in accordance with table 1 was prepared for the silanes which were not yet prehydrolyzed, the said mixture already containing the glacial acetic acid and ethanol, by prehydrolyzing at least one silane in acidic medium for at least three days at room temperature with stirring, where the silanes to be used were not already in prehydrolyzed form. Thereafter the silane already in prehydrolyzed form, where appropriate, was added, the system was stirred intensively and the preparation was stored at room temperature where appropriate. Thereafter the concentrates were diluted with water and, if desired, a pH modifier such as ammonia and/or glacial acetic acid was added in order to obtain treatment baths ready for use. Then in each case at least 5 sheets of cold-rolled steel (CRS) or of double-sidedly hot-dip-galvanized steel sheet were contacted by roller application and drying with the corresponding treatment liquid at 25°C. The metal sheets thus treated were dried at 90°C PMT and then tested for their corrosion protection. The compositions and properties of the concentrates and treatment baths and

also the properties of the coatings are summarized in tables 1 and 2.

Silanes A and B are fluorine-free, silane C is
5 fluorine-containing. Silane A is an amino-functional
trialkoxysilane which was hydrolyzed for only about two
hours before being added to the composition. Silane B
is a bis-trialkoxysilane which was hydrolyzed and
10 stored for about three days before being added to the
composition. Silane C is a water-soluble aminoalkyl-
functional fluoroalkylalkoxysilane which was added to
the composition only after a very long time of
hydrolysis and of storage. These details characterize
15 the constituent that is by far the most dominant in the
commercially available products. The silanes present
in the aqueous composition (concentrate or bath) are
monomers, oligomers, polymers, copolymers and/or
reaction products with further components owing to
20 hydrolysis reactions, condensation reactions and/or
other reactions. The reactions take place primarily in
the solution, during drying and, where appropriate,
curing of the coating. The term "silane" is used here
for silanes, silanols, siloxanes, polysiloxanes and
25 their reaction products and derivatives, which are
often "silane" mixtures. All of the concentrates and
baths proved to be stable for one week without changes
or precipitation. No ethanol was added. Amounts of
ethanol in the compositions originated only from
chemical reactions.

30

Polymer D is a readily filming thermoplastic polymer
based on ethoxylate. Polymer E is a polyethylene
copolymer. The SiO₂ particles had an average size of
approximately 200 nm. Monoethanolamine and/or ammonia
35 were added to the bath in order to adapt the pH.
Additionally, in the case of inventive/comparative
examples CE 10 and IE 11 to IE 20, an amount of
approximately 0.1 g/l of nonionic surfactant was added

in each case. This addition of surfactant helped in more effective wetting of the cleaned metallic surface. As a result, more uniform film formation was obtained, particularly in the case of metallic surfaces of
5 relatively complex shape or of particular roughness. Using these compositions, a coating with a dry film thickness of significantly less than 1 μm was produced.

Table 1: Compositions of high silane content: amounts in g/l for concentrates; remainder water

Inventive/ comparative examples	CE 1	CE 2	CE 3	IE 4	IE 5	IE 6	IE 7	CE 8	CE 9	CE 10	IE 11	IE 12	IE 13	IE 14	IE 15	IE 16	IE 17	IE 18	IE 19	IE 20
Organo- functional silane A	46	-	46	23	46	59	-	-	-	92	92	92	92	92	92	92	92	92	92	92
Organosilane B	-	95	95	48	95	122	-	-	-	190	190	190	190	190	190	190	190	190	190	190
F-silane C	-	-	-	4.3	8.5	1.7	4.3	8.5	17	-	17	34	102	17	34	17	17	34	34	17
Polymer D	-	-	-	-	-	-	-	-	-	-	-	-	-	100	200	-	-	-	200	100
Polymer E	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	100	-	-	-	-
SiO ₂ particles	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Glacial acetic acid	0.5	0.8	1.3	0.7	1.3	1.3	0.7	1.3	2.6	small amounts				added				ditto		
Ethanol	1.4	2.0	3.9	2.0	3.9	3.9	2.0	3.9	7.8	small amounts				added				ditto		

Table 2: Compositions of the treatment baths and properties of the dried coatings formed; remainder water; amounts in g/l

Inventive/ comparative examples	CE 1	CE 2	CE 3	IE 4	IE 5	IE 6	IE 7	CE 8	CE 9	CE 10	IE 11	IE 12	IE 13	IE 14	IE 15	IE 16	IE 17	IE 18	IE 19	IE 20
Organo- functional silane A	4.6	-	4.6	2.3	4.6	5.9	-	-	-	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
Organosilane B	-	9.5	9.5	4.8	9.5	12.2	-	-	-	19.0	19.0	19.0	19.0	19.0	19.0	19.0	19.0	19.0	19.0	19.0
F-silane C	-	-	-	0.43	0.85	0.17	0.43	0.85	1.7	-	1.7	3.4	10.2	1.7	3.4	1.7	1.7	3.4	3.4	1.7
Polymer D	-	-	-	-	-	-	-	-	-	-	-	-	-	10	20	-	-	-	20	10
Polymer E	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	10	-	-	-	-
SiO ₂ particles	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5	0.5	0.5	5
Glacial acetic acid	0.05	0.08	0.13	0.07	0.13	0.13	0.07	0.13	0.26	small amounts										added
Ethanol	0.14	0.20	0.39	0.20	0.39	0.39	0.20	0.39	0.78	small amounts										added
pH	10.1	3.3	5.7	5.9	5.8	5.9	4.3	4.2	4.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2	7.2
Contact angle in °																				
On steel sheets	88	35	76	106*	117	n.m.	n.m.	114	n.m.	n.m.	115	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
On HDG sheets	94	83	94	104	128	n.m.	n.m.	123	n.m.	n.m.	122	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Salts spray test: bright corrosion in R _i values after																				
1 h	3	2	2.5	2	<1	1	n.m.	3	n.m.	1.5	<<1	<<1	<<1	0	0	<1	<<1	<<1	0	0
5 h	5	5	5	4	<3	<3	n.m.	5	n.m.	4	<2	<1.5	1	1	<1	2	<2	<1.5	<1	<1

5 * outlier in the case of contact angle measurements

The films formed here were transparent, uniform and coherent. In all cases apart from CE 2, they showed no coloring on steel sheet. The structure, gloss and color of the metallic surface appeared to be changed only a little as a result of the coating. The combination of two or more silanes, including a relatively small fraction of a fluorine-containing silane, gave a marked improvement in corrosion protection, even when the amount of fluorine-containing silane added was comparatively small. In this case no further coating, in other words including no primer coat or varnish coat, had been applied to the silane coating. The corrosion protection values run from 0 to 5, with 5 representing the poorest values. The selection of the systems composed of fluorine-free silanes and/or of fluorine-containing silane showed its worth, since all of these combinations gave very stable solutions.

20 The film thickness of the coatings produced in this way - including the kind of application, which was varied to begin with - was in the range from 0.02 to 0.16 μm , mostly in the range from 0.02 to 0.12 μm .

25 The contact angle was measured using a DIGIDROP Contact Angle Meter from GBX Scientific Instruments using double-distilled water over 5 measurements per sheet. The greater the contact angles, the more hydrophobic the surface. In the case of experiment CE 2, in contradistinction to the other coated sheets, the steel sheet coated showed the color of golden rust, which had an adverse effect on the contact angle. Additionally it was found that the contact angle was determined not only by the silane applied, alone, but also by the effects of the surface treatment, such as the pH, for example. It emerged, surprisingly, that in the case of these experiments an amazingly strict correlation occurred between the hydrophobicity of the coated

surface, the contact angle, and the corrosion resistance of the coating system.

It was found that in many cases it is useful both to
5 give the surface of the coating certain hydrophobic
qualities - measurable from the contact angles - and to
ensure that the coating has a certain thickness, in
order to act as a corrosion protection barrier. The
silanes here improved attachment to the metallic
10 surface.

The coatings produced herewith are in many cases
suitable for coating with powder coating material or
with solvent-based paint. Water-based paint
15 compositions, in contrast, are repelled.

B) Compositions of after-rinse solutions substan-
tially based on silanes:

20 The aqueous solutions were prepared as in the case of
experiment series A), with the exceptions that the
compositions were chosen in accordance with table 3 and
the conversion-coated metal sheets based on the
aluminum alloy AA 6063 were coated by being immersed in
25 the bath solution for 1 minute at room temperature.

The sheets of aluminum alloy AA 6063 had been treated
beforehand with a conversion coating based on cerium-
rich rare earth compounds in accordance with WO-A1-
30 01/71058.

Table 3: Use of silane-rich solutions as after-rinse
solutions in comparison with the absence thereof or
with yellow chromate coating:

Inventive/ comparative examples	CE 21	IE 22	IE 23	IE 24	CE 25
Organofunctional silane A	-	-	65.2	-	-
Organosilane B	-	-	134.8	-	-
Organofunctional silane F	-	20	20	-	-
Nonfunctional silane G	-	-	-	50	-
F-silane C	-	3.4	3.4	5.1	-
Polymer D	-	-	30	-	-
Isopropanol	-	100	-	-	-
Nonionic surfactant	-	0.5	0.5	0.5	-
Glacial acetic acid	-	5.8	present	present	-
Ethanol	-	present	present	present	-
Monoethanolamine	-	-	to pH 7.2	-	-
Water	-	860	730	830	n.m.
pH	-	2.5	7.2	4.5	n.m.
After-rinse solution	no after- rinse	see above	see above	see above	yellow chromate coating
Salt spray test to DIN 50021 SS for					
24 h	OK	OK	OK	OK	OK
96 h	80-100% brownish black	OK	OK, but milky traces	OK	OK

The thicknesses of the coating of the invention produced with the after-rinse solution were from 0.2 to 0.3 μm . The coatings of the invention were transparent and slightly iridescent. They were highly uniform and very greatly enhanced the corrosion resistance of the underlying conversion coating based on cerium-rich oxides. The sheets of inventive examples IE 22 to IE 24, coated inventively with an after-rinse solution, had a corrosion resistance comparable with that of a conventional yellow chromate coating, without containing environmentally harmful substances. The expectations with regard to the improvement in corrosion resistance had been fulfilled more comprehensively than expected.